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# STUDIES ON SINGLET DELTA OXYGEN IN SUPPORT OF COIL

Final Scientific Report

AFOSR-82-0199 (a minigrant)

June 30, 1983

AFOSR-82-0199

by

Henry A. McGee, Jr.

Professor of Chemical Engineering and Principal Investigator

COIL FROM Pg. 1

Abstract

Although it is a highly reactive and dangerous species,  $\text{Cl}_2\text{O}$  is potentially more than twice as effective in reducing  $\text{H}_2\text{O}_2$  to  $\text{O}_2(^1\Delta)$  than is  $\text{Cl}_2$ . It has been conveniently and routinely synthesized from the reaction of  $\text{Cl}_2$  with  $\text{Na}_2\text{CO}_3$  in a fluidized bed reactor configuration. Conversions are of the order of 80 percent, and a typical rate in our facility of 6  $\text{cm}^3/\text{sec}$  of  $\text{Cl}_2$  yields 0.5 gm/min of  $\text{Cl}_2\text{O}$ . The now convenient production, handling, and analysis of  $\text{Cl}_2\text{O}$  was preliminary to our study of its efficacy in producing  $\text{O}_2(^1\Delta)$ .

Keywords: Chemical  
Oxygen-Iodine Laser

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## INTRODUCTION

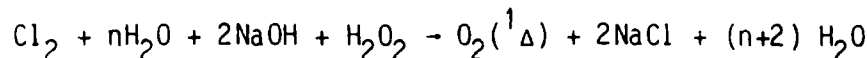
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→ In significant measure, COIL is an exercise in chemical engineering. The traditional chemical engineering concerns of chemical reaction with simultaneous heat, mass, and momentum transport processes are evident in the optical cavity as well as in the upstream manufacture of  $O_2(^1\Delta)$ . The ultimate product of COIL is coherent radiation while much more usually, the chemical engineer is concerned with the production of some chemical compound, say penicillin, as a product. But the scientific issues are very similar. This Laboratory is concerned with all of the chemistry of COIL.

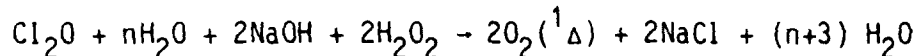
- ← COIL 1214
- the production of  $Cl_2O$
  - the efficacy of  $Cl_2O$  in the production of  $O_2(^1\Delta)$
  - the energy transfer from  $O_2(^1\Delta)$  to I to produce an inversion of highest possible number density.

This specific project was concerned only with the first of these interests, that is, with the design, construction, and operation of a reaction and purification facility for the routine production of  $Cl_2O$ .<sup>1</sup>

The goal is ultimately a more efficient and more compact COIL. At the present time,  $O_2(^1\Delta)$  is produced from basic peroxide by the reaction



whereas the reduction of peroxide with  $Cl_2O$  proceeds similarly

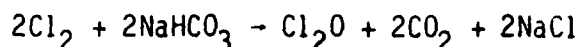
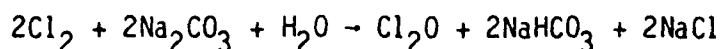


but wherein we see that one mole of chlorine oxide will produce two moles of  $O_2(^1\Delta)$  rather than one as is produced with chlorine itself. In addition to that,  $Cl_2O$  is five times more soluble in water than is  $Cl_2$ , and we anticipate a correspondingly greater solubility in basic peroxide as well.

Although the chemistry with peroxide is favorable,  $\text{Cl}_2\text{O}$  is a difficult and, in many ways, obnoxious substance. Some of its more fundamental properties are summarized below<sup>2</sup>:

Normal boiling point:  $2^\circ\text{C}$   
Freezing point:  $-120.6^\circ\text{C}$   
Heat of formation:  $18.1 \pm 0.3 \text{ kcal/mol}$  (273.15 K)  
Free energy of formation:  $21.95 \text{ kcal/mol}$  (273.15 K)  
Absolute entropy:  $63.76 \text{ cal/mol K}$  ( $25^\circ\text{C}$ )  
Fundamental absorption frequencies ( $\text{cm}^{-1}$ ) 684, 320, 973  
Nonlinear molecule with dipole moment of 1.83 Debyes  
Ionization potential:  $11.16 \pm 0.10 \text{ eV}$   
A pale orange-yellow gas that condenses to a reddish-brown liquid

Two general techniques were considered for the preparation of  $\text{Cl}_2\text{O}$ ; one involving reaction of chlorine with mercuric oxide and the second involving reaction of chlorine with sodium carbonate and perhaps related species. The mercuric oxide technique has the advantage of a convenient regeneration of  $\text{HgO}$  from the  $\text{HgCl}_2$  that is formed in the  $\text{Cl}_2\text{O}$  synthesis reaction. Thus a recycle or regenerative process can be designed. But this process also has the distinct disadvantage of using a highly poisonous powder. We elected to avoid the  $\text{HgO}$  process for that reason. The sodium carbonate process proceeds as follows,



This is also the industrial process in use for the production of chlorine oxide.

## PROCESS DEVELOPMENT

As is always the case, the development of a convenient and efficient process for the production a relatively unusual chemical has been an evolutionary process. In this Section, we briefly describe the major milestones in this evolutionary process development.

The first design of our production facility is shown schematically in Figure 1. The reactor is a section of 4 in. diameter glass pipe with a 3 ft. tall packed bed of lumps of  $\text{Na}_2\text{CO}_3$  pentahydrate. The lumps are up to about 0.5 in. in diameter. The tower contains 3 kg. of carbonate. Moisture is removed by passing the product stream through a tower of  $\text{P}_2\text{O}_5$  containing 0.5 kg. of the drying agent. The  $\text{Cl}_2\text{O}$  and unreacted  $\text{Cl}_2$  are condensed in the cold trap that is maintained at any temperature down to  $-78^\circ$ . The temperature of the trap is automatically maintained by a refrigerant circulating system using an L&N recorder/controller in a simple on-off control mode. Most of the unreacted  $\text{Cl}_2$  will pass through the condensation trap if it is maintained at  $-60^\circ\text{C}$ . The traces of  $\text{Cl}_2$  that do condense to contaminate the  $\text{Cl}_2\text{O}$  product can be removed by pumping on the liquid held at  $-78^\circ\text{C}$ .

The problem with this particular reactor configuration is the formation of salt ( $\text{NaCl}$ ) which can be seen growing on the surface of the sodium carbonate as the reaction proceeds. Thus the progress of the reaction in effect turns off the reaction. We then developed a fluidized bed process in which the fine particles of  $\text{Na}_2\text{CO}_3$  are in continuous violent agitation against each other such that the salt that is formed on the surface is abraded away to continuously expose fresh carbonate to the incoming chlorine. The schematic of this second evolution in the process development is very much like that of Figure 1, except now the nitrogen flow rate is very high to maintain the fluidized carbonate bed. The  $\text{N}_2$

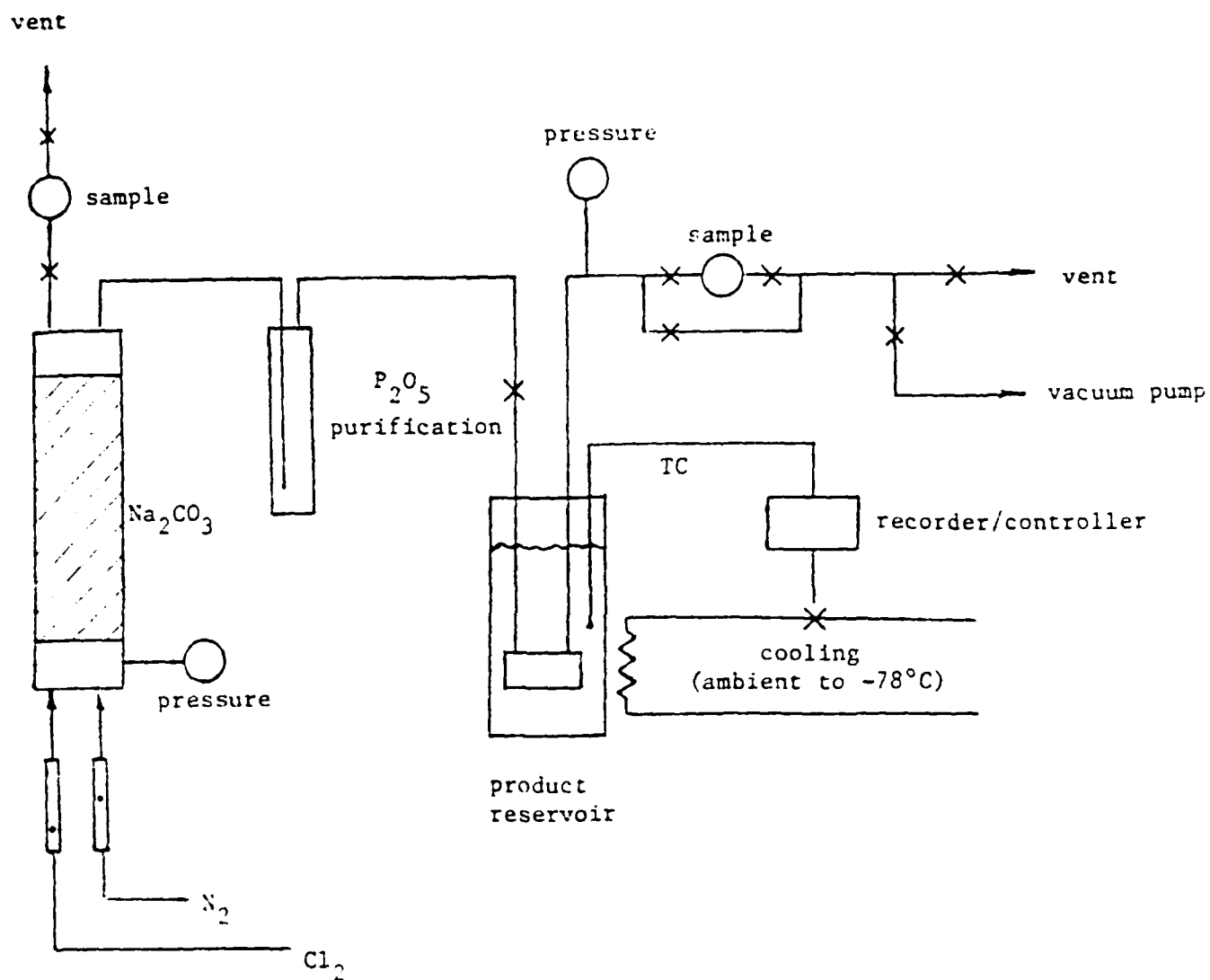


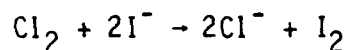
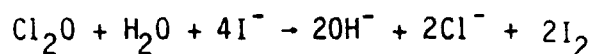
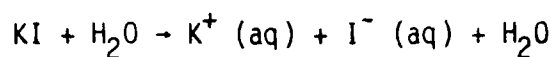
Figure 1: Schematic of facility developed for the production of  $\text{Cl}_2\text{O}$ .

flow is controlled with a stainless steel globe valve and the  $\text{Cl}_2$  is controlled with a monel needle valve. The flow rates of both gases are noted using previously calibrated rotameters. The gases are distributed across the cross-section of the bed by a stainless steel fritted plate. Approximately 1.5 kg of sodium carbonate provided a one-foot deep quiescent bed of solid. The maximum  $\text{N}_2$  flow rate to fluidize the bed was  $272 \text{ cm}^3/\text{sec}$ . The minimum rate was  $52 \text{ cm}^3/\text{sec}$ . In initial experiments, the product reservoir of Figure 1 was replaced by a simple carbon tetrachloride trap which removed all of the incoming  $\text{Cl}_2\text{O}$  and chlorine. Analysis of this solution suggested that the conversion was approximately 80%. The analysis is particularly convenient with the  $\text{Cl}_2\text{O}$  and  $\text{Cl}_2$  in  $\text{CCl}_4$  solution. Now the product of the titration is water which is insoluble in the  $\text{CCl}_4$  and the water then appears as a second phase floating on the  $\text{CCl}_4$ .

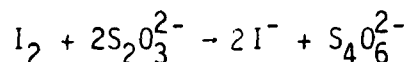
A difficulty with this latter configuration is the high nitrogen flow that is required to maintain the fluid bed. This large amount of gas rushing through the remainder of the flow system is troublesome. Therefore the third and final modification of the original process is that of use of an intermittent fluidized bed. Here the chlorine is admitted through a quiet bed and  $\text{Cl}_2\text{O}$  is formed. The chlorine is then closed off, the downstream system is closed, the reactor is vented, and the bed is fluidized with a heavy stream of nitrogen. This abrades away the salt, exposing fresh carbonate, the bed is then allowed to settle, and the gentle stream of chlorine readmitted. An alternative possibility here would be to merely gently stir the solid bed during the chlorine admission. This too should abrade away the salt.

## ANALYSIS

Monitoring of the synthesis process as well as the subsequent purification utilized both our Varian MAT 112 mass spectrometer as well as a conventional iodometric titration. For mass spectrometric analyses, a sample was captured in a 200 ml stainless steel sampling flask for subsequent manipulation. The wet chemical analysis utilized a titrimetric technique in which the  $\text{Cl}_2\text{O}$  reacts with iodide.<sup>3</sup> Either water or carbon tetrachloride was used as a solvent for the  $\text{Cl}_2\text{O}$  product in performing the iodometric analyses. Chlorine monoxide and chlorine liberate iodine from iodide as follows:

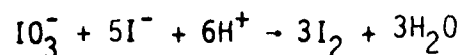


A known excess of acid (usually acetic acid) must be added to neutralize the  $\text{OH}^-$  ion. Iodine in solution has a bright yellow color, so it is easily titrated using sodium thiosulfate by the following reaction:



Soluble starch solution was used as an indicator at low iodine concentrations. The blue-violet color that is produced allows for sharp end-point determinations. The presence of the  $\text{OH}^-$  ion is useful when titrating solutions of both  $\text{Cl}_2\text{O}$  and  $\text{Cl}_2$ , for a back titration can be performed to determine the amount of residual acid. Excess potassium iodate is added to liberate iodine for the back titration by the following chemistry:

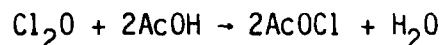




The iodine is again titrated with sodium thiosulfate. Thus, the first titration determines both the amount of  $\text{Cl}_2\text{O}$  and  $\text{Cl}_2$ , while the back titration determines the amount of chlorine monoxide alone.

Iodometric titrations can also be performed in carbon tetrachloride solutions. There are two benefits in using  $\text{CCl}_4$  as a solvent. One benefit is that more concentrated solutions are obtained with  $\text{CCl}_4$ , since chlorine monoxide is more soluble in  $\text{CCl}_4$  than in water. The second benefit is that iodine has a bright violet color in solution with  $\text{CCl}_4$ , even at low iodine concentrations. Therefore, sharp end-points are obtained without the use of an indicator such as soluble starch. Both iodometric titrations are quantitative.

The chemical test involving anhydrous acetic acid is only qualitative and is only suitable for carbon tetrachloride solutions. The chemistry is illustrated below:



When  $\text{Cl}_2\text{O}$  is present in the  $\text{CCl}_4$ , an aqueous phase will appear floating on the  $\text{CCl}_4$  phase. This "quick and dirty" qualitative test was convenient and frequently used.

#### PERSONNEL

The process development for the manufacture of  $\text{Cl}_2\text{O}$  has formed the MS thesis of Mr. John Hain. Mr. Hain was educated in Chemistry at the Coast Guard Academy and was a dual major in chemistry and mathematics at SUNY-Albany before joining this Department as a graduate student seeking to develop expertise in chemical engineering built upon his baccalaureate education in pure chemistry. This is a difficult transition, it requires

approximately a year of remedial work in the undergraduate core courses in chemical engineering and Mr. Hain has accomplished all of this in good order. A copy of the thesis will be submitted to AFOSR when its preparation is completed in a few weeks.

#### CONCLUSIONS

The reaction of chlorine with sodium carbonate in a fluidized bed reactor provides an efficient and convenient process for the production of chlorine oxide. In typical laboratory-size preparations, 1.5 kg of sodium carbonate is fluidized in a 4 in. ID glass reactor with nitrogen flowing at  $270 \text{ cm}^3/\text{sec}$  (STP) with a simultaneous injection of chlorine at about  $6 \text{ cm}^3/\text{sec}$  (STP). The reaction operates at room temperature and the conversion to chlorine oxide is approximately 80%.

#### FUTURE WORK

With the production of chlorine oxide conveniently in hand, we will be exploring now the efficacy of this reagent in producing singlet delta oxygen from peroxide as mentioned in the Introduction. Detection of the oxygen is by monitoring the dimol emission at  $1.27 \text{ }\mu\text{m}$  using a liquid nitrogen cooled germanium detector. This detector must be calibrated against an ESR machine, and our calibration is not yet complete. We are presently theoretically examining a number of reactor configurations and designs in an attempt to achieve the optimum balance between gas-liquid contacting on the one hand with removal of a fragile and continuously decomposing product species on the other hand. This is, of course, an old problem in chemical engineering generally as well as in this particular system, and it has been studied by a number of investigators in the recent past.<sup>4,5,6</sup> As initial "proof" experiments with the chlorine oxide we plan

to merely duplicate the Rocketdyne reactor<sup>4</sup> which has been shown to be rather efficient. With success there, a new engineering analysis for improved reactor design with  $\text{Cl}_2\text{O}$  will be carried out.

In the final analysis, if COIL is to be more efficient than with present technology, we must produce high number densities of  $\text{O}_2(^1\Delta)$  and I atoms in the optical cavity. This is also a problem in chemical engineering reactor design which we are also now considering.

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